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(54) Aqueous Latex Adhesive Compositions

(57) The compositions comprise an emulsion of at least one elastomeric copolymer of

(1) at least one monomer selected from the group consisting of 2-halobutadiene-1,3 and 2,3-dihalobutadiene-1,3; and

(2) at least one monomer selected

from the group consisting of α -haloacrylonitrile, α -haloacrylic acid, α -haloacrylic ester, α -halovinyl ketone, α -halovinyl acetate, vinyl halide and vinylidene halide (the halogen in monomers 1 and 2 being Cl, Br or F); said emulsion having optionally suspended therein at least one aromatic poly-C-nitroso compound. The emulsions are useful for bonding natural and synthetic elastomers to rigid and non-rigid substrates.

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SPECIFICATION

Aqueous Organic Compositions

This invention relates to water-based organic compositions. More particularly, the invention relates to water-based organic polymer-containing compositions especially suitable as adhesives for bonding natural and synthetic elastomers to rigid and non-rigid substrates.

The use of adhesive compositions for bonding natural and synthetic elastomers to the same or different elastomers, as well as to non-rigid and other rigid substrates, including metals, wood, ceramics, natural and synthetic organic and inorganic fibers, and the like, to form laminates and composite articles is well-known. To meet the operational requirements imposed by commercial considerations in bonding elastomers to rigid and non-rigid substrates, there have been developed any number of adhesive formulations which have enjoyed some measure of commercial success, with no single formulation being the panacea which provides optimum results in all bonding applications. In the general case, adhesives for bonding elastomeric materials to rigid substrates are organic solvent-based, i.e., the adhesive ingredients, including film-forming materials, are dissolved in or dispersed into organic solvents. Solvent-based adhesives are employed to a lesser extent for bonding elastomeric materials to non-rigid substrates, particularly synthetic fiber substrates, since these latter substrates generally do not adhere adequately to natural and synthetic elastomers without special treatment, such as the application of an adhesive composition comprising a water-based latex-resin composition.

Although generally exemplary for bonding applications with respect to elastomeric materials, solvent-based adhesives systems do have several drawbacks. For example, many of the known adhesives are lacking in versatility, i.e., though useful in bonding specific elastomers to specific substrates, the adhesive compositions are not capable of being utilized with a wide variety of elastomers and/or substrates. Another very serious drawback is the high cost of the solvents systems, which quite often cannot be reclaimed without prohibitively costly recovery systems. The increasing scarcity of petroleum from which the solvents are derived, and the apparent upward continued escalation in cost of petroleum stocks promises even higher costs for solvent-based adhesive systems. A further drawback with solvent-based adhesives is the plethora of federal, state and local legislation in the areas of environmental safety, occupational safety and the consumer product safety. While the latter two areas apply to adhesive systems generally, the field of environmental protection regulations is directed primarily to solvent-based adhesives since such regulations are concerned with restrictions on the type and quality of emissions to the atmosphere.

Quite obviously, water-based adhesive compositions, i.e., the adhesive ingredients are soluble in or dispersed into water, appear less susceptible to conflict with environmental protection regulations than solvent-based systems. Water-based adhesive systems are known but their use has been principally in applications wherein at least one substrate is porous or can absorb water, and which are not so hydrophobic as to interfere with or inhibit coalescence of the adhesive film former. Because of the economic and environmental advantages which the promised by water-borne systems, there is being expended a significant effort by the adhesive industry to develop water-based adhesives which can approach the performance of solvent-based adhesives.

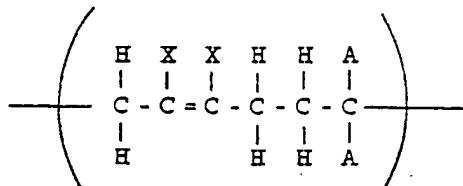
Generally, solvent-based adhesives systems which are in most demand by industry in elastomer-bonding areas are characterised by an extended shelf stability, i.e., they can be stored for indefinite periods without undue gelation or loss of adhesive capabilities; have good layover stability, i.e., parts can be coated with wet adhesives, dried and stored for indefinite periods without substantial loss of adhesiveness; and the adhesive is heat-activatable, i.e., the active adhesive materials remain substantially inert until the bonded assembly is brought to the temperature at which the bonding is to be effected. In the case of elastomer bonding applications, this temperature is generally that at which vulcanization of rubber is effected.

While water-borne adhesive systems can provide adequate adhesion to some substrates, e.g., the aqueous resin-latex formulations such as resorcinol-formaldehyde-latex (RFL) systems employed in bonding rubber to tire cord, such compositions are notoriously deficient with respect to stability. For example, even the best of such systems must be used within about two weeks after being prepared before gelation and/or loss of adhesive capability occurs. Further deficiencies of water-borne adhesive systems include the failure of such compositions to provide a continuous adhesive film and, while in certain instances the adhesion provided between the elastomer and the rigid substrate is acceptable, the general order of adhesion provided is moderate to poor. Moreover, the resistance to heat, solvents and moisture of the bonds provided by the known water-based compositions, particularly when employed in rubber-to-metal bonding, is not as great as is normally desired in commercial applications. Thus, there remains a need for water-borne adhesive compositions which are stable for extended periods of time, retain their strength during storage, exhibit an adhesive strength comparable to commercial solvent-based adhesive systems, and can be employed with a variety of elastomers and/or substrates.

In accordance with the present invention, there are provided storage-stable, heat-activatable, one-package, water-based adhesive compositions which are especially suitable for bonding natural and synthetic rubbers to rigid and non-rigid substrates, and which provide adhesive strengths comparable

to commercial solvent-based adhesive systems. According to another aspect of the invention, there is provided a method for bonding natural and synthetic elastomers to the same of different elastomers and to rigid and non-rigid substrates.

- The adhesive compositions of the present invention comprise an aqueous suspension or
 5 dispersion of at least one elastomeric copolymer consisting essentially of the reaction product of
 (1) at least one halogenated conjugated diene first monomer selected from the group consisting
 of 2-halo-1,3-butadiene and 2,3-dihalo-1,3-butadiene; and
 (2) at least one α -halovinyl second monomer selected from the group consisting of α -
 haloacrylonitrile, α -haloacrylic acid, α -haloacrylic ester, α -halovinyl ketone, α -halovinyl acetate, vinyl
 10 halide and vinylidene halide;
 wherein
 (a) the amount of said second monomer comprises from 12 to 49 percent by weight of said
 elastomeric copolymer;
 (b) the halogen moiety of said first and second monomers is selected from the group consisting of
 15 chlorine, bromine and fluorine;
 (c) said elastomeric copolymer has as an essential and characteristic feature a plurality of units
 having the structure



- characterized by the presence of at least one $S_{\text{N}}2$ labile halogen atom; wherein X is selected from the
 20 group consisting of chlorine, bromine and fluorine and is preferably bromine; and A is selected from the
 group consisting of $-\text{C}\equiv\text{N}$, $-\text{COOH}$, $-\text{COOR}^1$, $-\text{COR}^2$, $-\text{OOCOR}^3$, hydrogen, chlorine, bromine and
 fluorine and R^1 , R^2 and R^3 are alkyl radicals having from 1 to 8 carbon atoms;
 (d) said elastomeric copolymers has a halogen content in the range from 7 to 48, preferably 12 to
 37, weight percent, and
 25 (e) said adhesive composition has a total solids content, based on weight of elastomeric
 copolymer, in the range from 5 to 50 percent by weight. Optionally, and preferably, the adhesive
 compositions of the invention will have dispersed therein from 1 to 200, preferably 1 to 100, parts by
 weight, based on total weight of adhesive ingredients, of at least one aromatic poly-C-nitroso
 30 compound. The adhesive compositions of the invention can also have optionally included therein from
 10 to 90 percent by weight of at least one water-soluble or water-dispersible auxiliary film-forming
 material selected from the group consisting of halogenated rubber, halogenated resins and phenolic
 resins, said percentage being based on total weight of said elastomeric copolymer and said auxiliary
 film-forming material. The adhesive capability of the invention compositions is particularly surprising in
 35 view of the fact that aqueous latices of natural and synthetic rubbers such as acrylonitrile-butadiene
 and butadiene-styrene rubbers exhibit substantially no adhesive capability and the incorporation of
 additives such as dinitrosobenzene are not only ineffective in improving adhesion of such latices but
 also provides compositions which gel in a relatively short time. It is equally surprising to discover that
 the halogen-containing copolymers described herein provide effective water-based adhesive
 40 compositions since similar prior art halogen-containing polymers and copolymers require solvation in
 organic solvents in an amount of at least 5 weight percent before any effective adhesion could be
 obtained.

- The elastomeric copolymers which are employed in the present invention must be prepared by
 emulsion polymerization, that is, the halogenated conjugated diene and α -halovinyl comonomers are
 emulsified in an aqueous medium employing anionic emulsifying agents alone or an admixture of ionic-
 45 nonionic emulsifying agents, with such mixtures of ionic-nonionic emulsifying agents being currently
 preferred. It has been found that the elastomeric products best suited for use in the invention
 compositions contain from 51 to 88, preferably from 57 to 76, and, optimally, 64 to 72, percent by
 weight of first monomer (halogenated conjugated diene), and, correspondingly, from 12 to 49,
 preferably from 24 to 43, and, optimally, 28 to 36, percent by weight of second monomer (α -halovinyl
 50 compound). The amounts of conjugated diene first monomer and α -halovinyl second monomer can,
 however, extend beyond these limits.

- The emulsion polymerization is carried out in a closed vessel in which the space not occupied by
 the reaction mixture is preferably maintained free of oxygen by a blanket of inert gas, such as nitrogen.
 The induction period of the polymerization reaction is extended by the presence of oxygen and it is
 55 desirable to effect the reaction in the substantial absence of oxygen. In the broad sense, the emulsion
 polymerization is effected by mixing the monomeric ingredients, emulsifying this mixture, and
 subjecting the emulsion to moderate polymerization conditions until substantially all of the monomer
 charge has been polymerized. In the development of the adhesive systems, it was discovered that not

only is the micromolecular composition, that is, the polymeric composition relating to the amount of halogenated conjugated diene and α -halovinyl compound, important but also the macromolecular, that is, latex physical composition relating to particle size, also important, and both are directly related to the polymerization process. Thus, latices of similar microscopic composition, that is, similar

5 halogenated conjugated diene: α -halovinyl monomer ratios, prepared by different procedures can show large differences in rubber adhesion, as well as reproducibility of performance. While a conventional batch polymerization process wherein the comonomers are emulsified and the emulsion is allowed to polymerize to substantial completion can produce latices having good adhesion values, the process is highly inefficient due to the premature consumption of diene, resulting in significant amounts of

10 unreacted α -halovinyl monomer remaining in the latex and produces latices which provide more erratic bond results. A more efficient process is a procedure in which an emulsion of co-monomers rich in halogenated diene (75 to 100% of monomers) is added to an emulsion rich in α -halovinyl monomer (more than 60 percent of monomers). While latices having excellent adhesion can be prepared by this procedure, too slow an addition of the diene-rich emulsion, in order to aid in controlling the reaction

15 exotherm, yields latices having poor adhesion and film forming properties. Currently, it is preferred to effect polymerization at essentially steady state conditions of monomer starvation. This preferred method is a semi-continuous procedure in which an emulsion of halogenated conjugated diene and α -halovinyl monomer is added to a prepolymerized emulsion of identical composition. Slow addition of the comonomer emulsion is favored by this procedure as it is more likely to obtain the condition of

20 monomer starvation. Whereas conventional batch polymerizations result in the premature consumption of diene because of its greater reactivity, thereby resulting in unconsumed (unreacted) co-monomer, the preferred semi-continuous procedure maintains a constant or steady state ratio of diene to co-monomer in the reaction zone, which ratio is dependent on the ratio of diene to co-monomer in the feed emulsion and the relative reactivity of each, that is diene and co-monomer.

25 Polymerization conditions for batch and semi-continuous procedures are essentially the same and, as such, are well-known and need not be discussed here. With any procedure, it is preferred to employ reaction promoters such as free radical generating catalysts, such as ammonium persulfate and sodium dithionite, to assure more rapid onset of the reaction and more reproducible results. Other polymerization initiators which can be employed include alkali metal persulfates and perborates,

30 ammonium perborate, peroxides, such as hydrogen peroxide, benzoyl peroxide, and di-*t*-butyl peroxide and azo-bis(isobutyronitrile). If desired, conventional stabilizers can be included in the charge to the reaction vessel. Following the polymerization, unreacted monomer can be removed by vacuum treatment at elevated temperatures or steam distillation, with the specific method being a matter of choice.

35 Of prime importance to obtaining latices which provide acceptable adhesion is the choice of surfactants. It has been found that it is necessary to employ anionic surfactant agents or mixtures of anionic-nonionic surfactant agents. While cationic agents can be employed, their use, either alone or in combination with either or both anionic and nonionic agents, is detrimental to adhesive performance. The surfactant systems will be used in a range from 0.01 to 15 weight percent, preferably 1 to 10

40 weight percent, based on weight of monomers charged. The use of anionic-nonionic mixed surfactant systems is currently preferred, at a ratio of 1.2—2.1:1, preferably 1.3—1.8:1, anionic:nonionic agent. Representative anionic agents include carboxylates, such as fatty acid soaps from lauric, stearic and oleic acids, and acyl derivatives of sarcosine such as methyl glycine; sulfates, such as sodium lauryl sulfate (Duponol C); sulfated natural oils and esters, such as Turkey Red oil; alkyl aryl polyether

45 sulfates, such as Triton X-301; alkyl aryl polyether sulfonates, such as Triton X-200 and Ultrawet DS, K, 35K and 42K; isopropyl naphthalene sulfonates, such as Aerosol O5, and sulfosuccinates and sulfosuccinamates such as Aerosol OT, MA, TR, 102 and 18; phosphate esters, such as short chain fatty alcohol partial esters of complex phosphates (Victawet); and orthophosphate esters of polyethoxylated fatty alcohols (Gafac). Representative nonionic agents include ethoxylated (ethylene oxide derivatives of) mono- and polyhydric alcohols, such as the Triton octyl- and nonyl-phenol series;

50 ethylene oxide/propylene oxide block copolymers, such as the Pluronic series; esters, such as glyceryl monostearate; products of the dehydration of sorbitol, such as sorbitan monostearate and polyethylene oxide sorbitan monolaurate (Span and Tween series); and amides, such as lauric acid isopropanol amide (Lauridit LP). Currently preferred is a 1.5:1 mixture of sodium dodecylphenyl ether disulfonate

55 (Dowfax 2A1) anionic surfactant and nonylphenol polyethylene glycol nonionic surfactant. The anionic and anionic-nonionic surfactant systems which must be employed in the practice of this invention are described in more depth in "Emulsions: Theory and Practice", by Paul Becker, Chapter 6, Reinhold Publishing Corp., New York, 1965; and in McCutcheon's "Detergents and Emulsifiers, 1972 Annual".

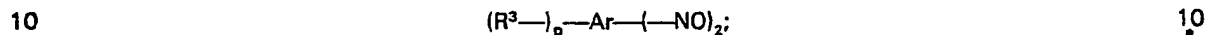
The aromatic nitroso compounds which are suitable for use in the practice of the present

60 invention can be any aromatic hydrocarbon such as benzene, naphthalene, anthracene and biphenyl which contains at least two nitroso groups attached directly to non-adjacent ring carbon atoms. More particularly, such nitroso compounds are described as poly-C-nitroso aromatic compounds having from 1 to 3 aromatic nuclei, including fused aromatic nuclei, having from 2 to 6 nitroso groups attached directly to non-adjacent nuclear carbon atoms. The presently preferred poly-C-nitroso materials are the

65 di-nitroso aromatic compounds, especially the di-nitroso benzenes and di-nitroso naphthalenes, such as

the meta- or paradinitrosobenzenes and the meta- or paradinitrosonaphthalenes. The nuclear hydrogen atoms of the aromatic nucleus can be replaced by alkyl, alkoxy, cycloalkyl, aryl, aralkyl, alkaryl, arylamine, arylnitroso, amino, halogen, and the like groups. The presence of such substituents on the aromatic nucleus has little effect on the activity of the poly-C-nitroso compounds in the present invention. As far as is currently known, there is no limitation as to the character of the substituents, which can be organic or inorganic in nature. Thus, where reference is made to poly-C-nitroso or di-C-nitroso "aromatic compound," "benzenes," or "naphthalenes", it will be understood to include both substituted and unsubstituted nitroso compounds, unless otherwise specified.

Particularly preferred poly-C-nitroso compounds have the formula



wherein Ar is selected from the group consisting of phenylene and naphthalene;

R^3 is a monovalent organic radical selected from the group consisting of alkyl, cycloalkyl, aryl, aralkyl, alkaryl, arylamine and alkoxy radicals having from 1 to 20 carbon atoms, amino, or halogen, and is preferably an alkyl group having from 1 to 8 carbon atoms; and

p is 0, 1, 2, 3, or 4 and is preferably 0.

A partial non-limiting listing of suitable poly-C-nitroso compounds which are suitable for use in the practice of the invention include m-dinitroso-benzene, p-dinitrosobenzene, m-dinitrosonaphthalene, p-dinitrosonaphthalene, 2,5-di-nitroso-p-cymene, 2-methyl-1,4-dinitrosobenzene, 2-methyl-5-chloro-1,4-dinitrosobenzene, 2-fluoro-1,4-dinitrosobenzene, 2-methoxy-1,3-dinitrosobenzene, 5-chloro-1,3-dinitrosobenzene, 2-benzyl-1,4-dinitrosobenzene, and 2-cyclohexyl-1,4-dinitrosobenzene.

Substantially any of the polymeric materials which have been heretofore employed as film formers or film-forming adjuncts in adhesive formulations are suitable for use in the practice of the present invention as auxiliary film-forming materials. Such film-forming materials include, without limitation, thermosetting condensation polymers, such as thermosetting phenolic resins, thermosetting epoxy resins, thermosetting polyester resins, thermosetting triazine resins, and the like; polymers and copolymers of polyethylenically unsaturated materials such as poly(vinylbutyral); poly(vinyl formal); poly(vinyl acetate); chlorinated poly(vinyl chloride); copolymers of vinyl acetate and vinyl chloride; chlorinated copolymers of vinyl acetate and vinyl chloride; polymers of acrylic acid; copolymers of acrylic acid and conjugated dienes, such as 1,3-butadiene; 2-chloro-1,3-butadiene; 2,3-dichloro-1,3-butadiene; and the like, and including after halogenated products thereof; polymers of methacrylic acid; copolymers of methacrylic acid and conjugated dienes; copolymers of vinylpyridine and conjugated dienes, and including polyvalent reaction products thereof; cellulosic materials such as cellulose acetate butyrate; and the like. Particularly preferred film-forming materials are halogen-containing rubbers, including without limitation, chlorinated natural rubber; polychloroprene; chlorinated polychloroprene; chlorinated polybutadiene; chlorinated polyethylene; chlorinated ethylene/propylene copolymers; chlorinated ethylene/propylene/non-conjugated diene terpolymers; chlorinated copolymers of butadiene and styrene; chlorosulfonated polyethylene; brominated poly(2,3-dichloro-1,3-butadiene); mixtures of such halogen-containing rubbers with hydrohalogenated rubbers of hypohalogenated rubbers; mixtures of two of more such halogen-containing rubbers and the like.

Other suitable polymeric film-forming adjuncts include cellulosic esters such as cellulose acetate butyrate; natural rubber; butyl rubber; ethylene/propylene copolymer (EPM) rubber; ethylene/propylene/diene terpolymer (EPDM) rubber; polymers and copolymers of dienes having from 4 to 12 carbon atoms, such as polybutadiene, and including also copolymers of such dienes of one or more different monomers copolymerizable therewith, such as SBR and butadiene/acrylonitrile rubber. As indicated halogenated polymeric materials, and particularly chlorinated and brominated rubbers, are preferred auxiliary film-forming materials. The relative ratios of elastomeric copolymer to auxiliary film-forming materials, when employed, is generally in the range from 10 to 90, percent by weight of elastomeric copolymer with a corresponding 90 to 10, preferably 80 to 10, percent by weight of auxiliary film-forming material.

The adhesive compositions of the present invention may also utilize fillers, extenders and coloring agent such as carbon black, as well as various metallic oxides, etc. These fillers are inert from the standpoint of affecting the adhesive properties of the compositions.

Generally, the solids content of the adhesive composition may range from as low as 5% to as high as about 50% solids.

A salient feature of the aqueous adhesive compositions of this invention is good shelf life, that is, can stability. Whereas conventional aqueous adhesives have relatively short (1 day—2 weeks) shelf life, the invention compositions have a shelf life in excess of two months. Another meritorious feature is that the invention compositions do not exhibit a decline in bonding ability when coated on a substrate and stored in air over a period of time. Neither does the bond between rubber and substrate (with the adhesive at the interface) deteriorate upon prolonged exposure to air.

The method of bonding natural and synthetic rubbers to rigid and non-rigid substrates using the curable adhesive composition of this invention generally comprises the steps of (1) making or preparing the above described aqueous adhesive composition; (2) coating the substrate with a thin

layer of the composition; (3) drying the adhesive coating such as by air drying or heating in an oven at slightly elevated temperatures; (4) contacting the adhesive coated substrate with a vulcanizable rubber composition; and (5) curing the adhesive concurrently with vulcanization of the rubber.

The adhesive compositions of the present invention prepared by conventional emulsification techniques which do not require further elucidation herein. 5

The following examples are provided to illustrate the invention. All parts and percentages which relate to composition are by weight unless otherwise indicated. In these examples, rubber adhesion is tested according to ASTM D-429, method B, modified to 45°. Adhesion values are reported in kilonewtons per linear meter, kN/m. Mode of failure is reported conventionally as R, CM, CP or the like, 10 with a numerical value indicating percent. Boiling water resistance is tested by immersing test samples in boiling water for two hours. Failure is determined by peeling rubber from metal with pliers immediately after removal from water. This test is more severe than standard tests in which the sample is cooled to ambient temperature before peeling. When the adhesive being tested is employed with a primer (2-coat adhesive systems), the metal parts are coated with the primer, allowed to dry, 15 coated with adhesive and again allowed to dry before being bonded to the elastomer stock. Otherwise, the unprimed metal parts are coated with adhesive and allowed to dry before being bonded to the elastomer stock. 15

Example I

Various commercially available latices are employed to bond solvent-wiped, grit-blasted, cold-rolled steel to sulfur-vulcanizable natural rubber stock. In each instance, the steel parts are coated with the latex composition and allowed to dry. The adhesively-coated parts are vulcanization-bonded to the sulfur-curable natural rubber composition at 153°C for 10 minutes. The test results are reported in the following table: 20

	<i>Latex</i>	<i>Adhesion, kN/m</i>	<i>Failure Mode</i>	
25	Chlorosulfonated polyethylene	PBH	100 CM	25
	Chlorosulfonated polyethylene w/10 wt. % dinitrosobenzene	4.6	100 RC	
	Polyurethane	PBH	100 RC	
	Neoprene	PBH	100 RC	
30	Poly(styrene-butadiene)	0.7	100 RC	30
	Carboxylated poly(styrene-butadiene)	3.8	20 RC, 80 CM	
	Carboxylated poly(styrene-butadiene) w/10 wt. % dinitrosobenzene	PBH	100 RC	
	Polyisoprene	PBH	100 RC	
35	Poly(vinyl pyridine)	0.7	100 RC	35
	Poly(acrylonitrile)	PBH	100 RC	

Example II

Pure 2,3-dichloro-1,3-butadiene is isolated from a commercial 50% methylene chloride solution by distilling off the methylene chloride and passing the residual monomer through an alumina column to remove inhibitor. The pure monomer is employed to prepare poly(2,3-dichloro-1,3-butadiene) latex according to the following recipe: 40

	Distilled water	1200 g	
	2,3-dichloro-1,3-butadiene	600 g	
	Sodium alkyl aryl ether sulfact anionic surfactant	60 g	
45	Ethoxylated octyl phenol nonionic surfactant	15 g	45
	Ammonium persulfate	0.5 g	
	Sodium dithionite	0.5 g	
	Ferrous sulfate, 0.15% solution	10 ml	

The 2,3-dichloro-1,3-butadiene is pre-emulsified under nitrogen in the usual fashion by high speed agitation in the water containing the surfactant mixture. The ammonium persulfate and sodium dithionite are then added and the resulting heat of reaction allowed to carry the temperature to 40°C. The polymerization exotherm is controlled by cooling to prevent the temperature from exceeding 40°C. After the main exotherm is over, the ferrous sulfate solution is added and the reaction mixture is allowed to polymerize overnight at ambient temperature. 50

The resulting latex is employed to bond solvent-wiped, grit-blasted, cold-rolled steel to natural and poly(styrene-butadiene) sulfur-vulcanizable elastomer compositions. The steel parts are coated with a solvent-based heat-reactive phenol resin primer prior to application of the adhesive. The assemblies are cured at 153°C, at variable cure times. Peel adhesion tests of the bonded assemblies are effected according to ASTM D-420, Method B, modified to 45°. The results are reported in the following table: 55

	<i>Elastomer Stock</i>	<i>Cure Time, Min</i>	<i>Peel Adhesion, kN/m</i>	<i>Failure Mode</i>	
	Natural Rubber	20	PBH	100 CP	
		30	PBH	100 CP	
5		40	PBH	100 CP	5
		50	PBH	100 CP	
	Poly(styrene-butadiene) rubber (SBR)	20	3.4	100 CP	
		30	3.8	100 CP	
		40	4.3	100 CP	
10		50	4.2	100 CP	10

The addition of 15 parts by weight, per 100 parts by weight of poly(2,3-dichloro-1,3-butadiene), of dinitrosobenzene provides an adhesive which when employed over solvent-based heat-reactive phenolic resin to bond solvent-wiped, grit-blasted, cold-rolled steel to sulfur-vulcanizable natural rubber, affords an adhesion value 3.8 kN/m, 100 RC.

15 Example III

A mixture of 600 g 2,3-dichloro-1,3-butadiene and 120 g α -chloroacrylonitrile is pre-emulsified in 100 ml distilled water with a mixed surfactant system (60 g sodium alkyl aryl ether sulfate anionic surfactant and 15 g ethoxylated octylphenol nonionic surfactant) under an atmosphere of nitrogen. To the pre-emulsion is added 0.5 g ammonium persulfate and 0.5 g sodium dithionite. The polymerization exotherm is controlled by cooling to less than 40°C. After the main exotherm is over, 10 ml of 0.15% ferrous sulfate solution is added and the reaction mixture is allowed to polymerize overnight at ambient temperature. The copolymer has a conjugated diene:halovinyl ratio of 5:1.

The resulting latex is employed to bond solvent-wiped, grit-blasted, cold-rolled steel to sulfur-vulcanizable natural rubber compositions. The steel parts are coated with solvent based, heat-reactive phenolic resin primer prior to application of the adhesive. The assemblies are cured at 153°C for 15 minutes. Peel adhesion tests are made as in Example II. An adhesion value of 6.3 kN/m, 15 R 25 RC failure mode, is obtained. The addition of 15 parts by weight, per 100 parts by weight of copolymer, dinitrosobenzene provides an adhesive which affords an adhesion value of 10.3 kN/m, 100 R.

Example IV

30 Copolymer latices are prepared as follows:

A. Batch Polymerization

A reaction vessel is charged with 3.2 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant, 2.4 g ethoxylated octylphenol nonionic surfactant and 90 g distilled water. The resulting solution is deoxygenated by a nitrogen stream and the monomers, 2,3-dichloro-1,3-butadiene (DCD) and 15 g α -chloroacrylonitrile (α -clan) are added. The mixture is emulsified by vigorously stirring and the initiators (ammonium persulfate, 0.3 g and sodium dithionite, 0.3 g) are added, producing an exothermic reaction which is controlled by external cooling to prevent the temperature from exceeding 60°C. After the initial exotherm has subsided, the reaction mixture is permitted to polymerize for 15 hours at ambient temperature. The resulting copolymer latex has a 3:1 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition.

B. Batch-1 Polymerization

A reaction vessel is charged with 1.6 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant, 2.4 g ethoxylated octylphenol nonionic surfactant and 30 g distilled water. The resulting solution is deoxygenated by a nitrogen stream and the monomers, 2,3-dichloro-1,3-butadiene (1.3 g) and α -chloroacrylonitrile (26 g), are added. The mixture is emulsified by vigorous stirring. Ammonium persulfate (0.2 g) and sodium dithionite (0.2 g) are added and the reaction mixture is heated to 60°C. To the heated reaction mixture there is added, at a constant rate over the course of 45 minutes, separately but simultaneously, (1), an emulsion consisting of 2.3 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant, 1.5 g ethoxylated octyl phenol nonionic surfactant, and 63 g 2,3-dichloro-1,3-butadiene in 51 g water, and, (2), a solution consisting of 0.25 g ammonium persulfate, 0.2 g sodium metabisulfite and 0.5 g sodium pyrophosphate in 20 g distilled water. After additions are complete, the reaction mixture is heated for 90 minutes at 60°C. The resulting copolymer latex has a 2.9:1, 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition.

C. Batch-2 Polymerisation

55 A copolymer latex having a 2.9:1 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition is prepared according to the Batch-1 polymerization method of this example, except that the addition to the heated reaction mixture of comonomer emulsion and initiator solution is accomplished over the course of 75 minutes.

D. Semi-Continuous-1 Polymerization

A reaction vessel is charged with 6.9 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant, 4.6 g ethoxylated nonylphenol nonionic surfactant and 172 g distilled water. The admixture is deoxygenated by a nitrogen stream and 129 g 2,3-dichloro-1,3-butadiene and 42 g α -chloroacrylonitrile are added. The resulting mixture is emulsified with vigorous stirring. To this emulsion is added 0.5 g ammonium persulfate and 0.5 g sodium dithionite. The reaction exotherms to 45°C. After the initial exotherm, the contents of the reaction vessel are heated at 55°C for 75 minutes. There is then added, at a constant rate over the course of 5 hours, separately but simultaneously, (1), an emulsion consisting of 74 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant, 49.1 g ethoxylated nonylphenol nonionic surfactant, 1420 g 2,3-dichloro-1,3-butadiene, and 465 g α -chloroacrylonitrile in 1828 g distilled water, and, (2), a solution consisting of 8 g sodium pyrophosphate, 4 g ammonium persulfate and 4 g sodium metabisulfite in 333.3 g distilled water. During the addition of the comonomer emulsion and the activator solution, the reaction temperature is kept in the range of 55–60°C. After the additions are completed, heating of the contents of the reaction mixture is continued for 90 minutes at 55°C. There is then added over the course of 45 minutes 100 g 2,3-dichloro-1,3-butadiene emulsified in 90 g distilled water containing 3.75 g disodium dodecyl diphenyl ether disulfonic acid anionic surfactant and 2.5 g ethoxylated nonyl phenol nonionic surfactant. Simultaneously, a solution consisting of 0.6 g sodium pyrophosphate, 0.3 g ammonium persulfate and 0.3 g sodium metabisulfite in 25 g distilled water is added to the polymerization zone. After the additions are complete, the reaction mixture is heated an additional 90 minutes at 55°C. The resulting copolymer latex has a 3.25:1 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition.

E. Semi-Continuous-2 Polymerization

A copolymer latex having a 3.25:1 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition is prepared according to the Semi-Continuous-1 Polymerization method of this example, except that the addition to the reaction zone of comonomer emulsion and activator solution is accomplished over the course of 2-1/2 hours, rather than 5 hours as in the Semi-Continuous-1 Polymerization.

Example V

A series of latices prepared according to polymerization methods A–E, inclusive, of Example are employed to bond solvent-wiped, grit-blasted, cold-rolled steel to sulfur-vulcanizable poly(styrene-butadiene) rubber compositions. The steel parts are coated with solvent-based, heat-reactive phenolic resin primer prior to application of the adhesive. The assemblies are cured at 153°C for 30 minutes. Adhesion tests are made as in Example II, with the results being reported in the following table:

Effect of Method of Latex Preparation on Adhesion

Method of Preparation	Ratio, 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile	Adhesion kN/m	Failure Mode
Batch	3:1	9.3	100 RC
Batch-1	2.9:1	22.1	50 R, 50 RC
Batch-2	2.9:1	5.5	80 RC, 20 ADH
Semi-Continuous-1	3.1:1	25.4	97 R, 3 RC
Semi-Continuous-2	3.05:1	11.0	50 SR, 50 RC

Example VI

A poly(2,3-dichloro-1,3-butadiene/ α -chloroacrylonitrile) latex at 46% solids and having a 2.5:1 2,3-dichloro-1,3-butadiene: α -chloroacrylonitrile composition is prepared by the Semi-Continuous-1 procedure of Example 4(d), using 1.9 part by weight, per 100 parts by weight of comonomers, of the mixed anionic-nonionic surfactants. The latex is divided into aliquot portions, and one portion is coagulated by pouring into methanol with rapid agitation. The precipitated polymer is washed in methanol, filtered and air-dried. The dried polymer is dispersed into a 3:1 toluene-methyl ethyl ketone solvent mixture. The aqueous and solvent systems are employed to prepare adhesives:

Adhesive A: Poly(2,3-dichloro-1,3-butadiene/ α -chloroacrylonitrile) latex at 46% solids.

Adhesive B: Poly(2,3-dichloro-1,3-butadiene/ α -chloroacrylonitrile) copolymer in toluene-methyl ethyl ketone solvent at 15% solids.

Adhesive C: Poly(2,3-dichloro-1,3-butadiene/ α -chloroacrylonitrile) latex at 46% solids plus 15 parts by weight, per 100 parts by weight, of copolymer, dinitrosobenzene.

Adhesives A, B, and C are employed to bond solvent-wiped, grit-blasted, cold-rolled steel to sulfur-vulcanizable poly(styrene-butadiene) rubber compositions. The steel parts are coated with

solvent-based heat-reactive phenolic resin primer prior to application of the adhesive. The assemblies are cured at 153°C for 30 minutes. Adhesive C is also employed to bond identically-prepared steel to sulfur-vulcanizable natural rubber compositions, with curing being effected at 153°C for 15 minutes. Adhesive C is employed as a freshly prepared composition and after aging for six weeks at 52°C,

5 adhesion tests are made as in Example II, with the results being reported in the following table: 5

	<i>Adhesive</i>	<i>Elastomer</i>	<i>Adhesion, kN/m</i>	<i>Failure Mode</i>	
	A	Synthetic ^a	30	97 R, 3 RC	
	B	Synthetic ^a	18.8	90 TR, 10 RC	
10	C ^b	Synthetic ^a	29.8	100 R, SB	10
	C ^b	Natural	8.8	100 R	
	C ^c	Synthetic ^a	25.6	100 R, SB	
	C ^c	Natural	10	100 R	

a=Poly(styrene-butadiene) rubber

15 b=Unaged adhesive 15

c=Adhesive aged 6 weeks at 52°C

Claims

1. A heat-activatable adhesive composition for bonding natural and synthetic rubbers to rigid and non-rigid substrates comprising
 - 20 a) an oil phase consisting essentially of
 - i) at least one elastomeric copolymer of a first monomer selected from the group consisting of 2-halo-1,3-butadiene and 2,3-dihalo-1,3-butadiene and a second monomer selected from the group consisting of α -haloacrylonitrile, α -haloacrylic acid, α -haloacrylic ester, α -halovinylketone, α -halovinyl acetate, vinyl halide and vinylidene halide; wherein the halogen moiety of said first and second
 25 monomers is selected from the group consisting of chlorine, bromine and fluorine and the amount of said second monomer comprises from 12 to 49 weight percent of said elastomeric copolymer and said elastomeric copolymer is prepared by emulsion copolymerization of said first and second monomers.
 - ii) at least 1 part by weight, per 100 parts by weight of active adhesive ingredients, of at least one aromatic nitroso compound; and
 30
 - iii) a surfactant system selected from the group consisting of anionic surfactant agents and a mixture of anionic and nonionic surfactant agents, the amounts of said surfactant system being in the range from 0.01 to 15 parts by weight, per 100 parts by weight of said first and second monomers and wherein, in said mixture of anionic and nonionic surfactant agents, the amount of said anionic surfactant agent is in the range from 1.2 to 2.1 parts by weight per part by weight of said nonionic
 35 surfactant agent; and
 - b) a water phase including water in an amount to provide an adhesive latex composition having a total solids content in the range from 5 to 50 percent.
 2. An adhesive composition according to claim 1 wherein the amount of said aromatic nitroso compound is in the range from 1 to 200 parts by weight.
 - 40 3. An adhesive composition according to claim 2 wherein the amount of said surfactant system is in the range from 1 to 10 parts by weight.
 4. An adhesive composition according to claim 2 wherein said oil phase contains at least one auxiliary film-forming material selected from the group consisting of halogenated rubber, halogenated resins and phenolic resins, the amount of said film-forming material being in the range from 10 to 90
 45 percent by weight, based on total weight of said elastomeric copolymer and said auxiliary film-forming material.
 5. An adhesive composition according to claim 2 wherein said first monomer is 2,3-dichloro-1,3-butadiene.
 6. An adhesive composition according to claim 5 wherein said second monomer is α -chloroacrylonitrile.
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 7. An adhesive composition according to claim 3 wherein said surfactant system comprises an admixture of at least one anionic surfactant agent and at least one nonionic surfactant agent.
 8. An adhesive system according to claim 7 wherein said first monomer comprises 2,3-dichloro-1,3-butadiene and said second monomer comprises α -chloroacrylonitrile.
 - 55 9. An adhesive composition according to claim 9 wherein the amount of said second monomer is in the range from 28 to 36 percent by weight. 55